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60/734,637 8 November 2005 (08.11.2005) US
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(54) Title: PROCESS FOR THE MANUFACTURE OF DICHLOROPROPANOL BY CHLORINATION OF GLYCEROL

(57) Abstract: Process for the manufacture of dichloropropanol by chlorination of glycerol Process for the manufacture of dichloropropanol in which glycerol is reacted with a chlorinating agent comprising hydrochloric acid in a liquid medium in equilibrium with a vapour phase and in which the condensation of a fraction exhibiting the composition of the vapour phase is prevented.

Process for the manufacture of dichloropropanol by chlorination of  
glycerol

The present patent application claims the benefit of provisional US patent application 60/734637 filed on 8 November 2005, the content of which is incorporated herein by reference.

5 The present invention relates to a process for the manufacture of dichloropropanol in which glycerol and a chlorinating agent are reacted optionally in the presence of an organic acid, so as to obtain reaction products comprising dichloropropanol. The dichloropropanol can be separated from the other reaction products and can be subjected to a dehydrochlorination reaction, so as to manufacture epichlorohydrin. Such a process is disclosed in Application  
10 WO 2005/054167 of SOLVAY SA, the content of which is incorporated in the present application by reference. A preferred chlorinating agent is hydrogen chloride.

In this process, the reaction between glycerol and the chlorinating agent is preferably carried out in a reactor and related ancilliary equipments made of or  
15 coated with materials resistant to chlorinating agents and in particular to hydrogen chloride under the reaction conditions. Enamelled (glass-lined) steel is a preferred vessel material. The applicant has found that such materials remain however unsatisfactory, i.e. they are corroded by liquid mixtures containing water, dichloropropanol and hydrogen chloride, resulting from the condensation  
20 of rich hydrogen chloride content vapours on the inner walls of the reactor and of related ancilliary equipments.

This aim of this invention is to provide a process for manufacturing dichloropropanol which does not exhibit that problem.

25 The invention therefore relates to a process for the manufacture of dichloropropanol in which glycerol is reacted with a chlorinating agent comprising hydrogen chloride, wherein, in a vessel, a liquid medium is in equilibrium with a vapour phase and wherein at least one part of the inner wall of the vessel which is above the level of the liquid medium in the vessel is maintained at a temperature lower than 120 °C or at a temperature at least 1 °C  
30 higher than the dew temperature of the vapour phase and/or is trickled with a liquid.

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The part of the inner wall of the vessel which is above the level of the liquid medium in the vessel is maintained at the required temperature continuously or intermittently.

5 The temperature of 120 °C is the temperature at which corrosion of enamelled steel at a rate of at least 0.01 mm/year is observed in the presence of hydrogen chloride/water liquid mixtures containing at least 4 % by weight of hydrogen chloride.

10 The vessel can be any vessel of the process for manufacturing the dichloropropanol where the temperature of the liquid phase is higher than 120 °C, like for instance a reactor, a distillation column, a stripping column or a decantor.

15 It has now been found that by working under such conditions of temperature and/or wetting conditions the corrosion of the inner vessel wall above the level of the liquid medium can be reduced. Without wishing to be bound by any theory, it is believed that when the temperature of the inner wall of the vessel which is above the level of the liquid medium in the vessel is lower than 120 °C, the corrosion rate is reduced even in contact with very corrosive condensed mixtures containing water, hydrogen chloride and dichloropropanol. It is also believed that when the temperature of the inner wall of the vessel which is above the level of the liquid medium in the vessel is at a temperature at least 1 °C higher than the dew temperature of the vapour phase above the liquid medium, the corrosion rate is reduced due to a reduced condensation of vapours containing water, hydrogen chloride and dichloropropanol. Finally, it is also believed that when the inner wall of the vessel which is above the level of the liquid medium in the vessel is trickled with a liquid, the corrosiveness of condensed mixtures containing water, hydrogen chloride and dichloropropanol is reduced by dilution. The reduction of the corrosion of the constituent materials of the vessel makes it possible to further limit the costs associated with the replacement of the latter.

30 In the liquid corrosive mixtures obtained by condensation of the vapours containing water, hydrogen chloride and dichloropropanol, the hydrogen chloride content is generally higher than or equal to 1 % by weight of the mixture, frequently higher than or equal to 3 % and often greater than or equal to 5 %. The hydrogen chloride content is generally lower than or equal to 80 % by weight of the mixture, frequently lower than or equal to 60 % and often lower than or equal to 50 %.

In the liquid corrosive mixtures obtained by condensation of the vapours containing water, hydrogen chloride and dichloropropanol, the water content is generally higher than or equal to 4 % by weight of the mixture, frequently higher than or equal to 5 % and often greater than or equal to 10 %. The water content  
5 is generally lower than or equal to 80 % by weight of the mixture, frequently lower than or equal to 70 % and often lower than or equal to 60 %.

In the liquid corrosive mixtures obtained by condensation of the vapours containing water, hydrogen chloride and dichloropropanol, the dichloropropanol content is generally higher than or equal to 4 % by weight of the mixture,  
10 frequently higher than or equal to 5 % and often greater than or equal to 10 %. The dichloropropanol content is generally lower than or equal to 80 % by weight of the mixture, frequently lower than or equal to 70 % and often lower than or equal to 60 %.

Others compounds can also be present in the liquid corrosive mixtures containing water, hydrogen chloride and dichloropropanol, like for instance  
15 glycerol, monochloropropanediol, and esters thereof.

The level of the liquid medium in the vessel is defined as the level of the liquid when the vessel is operating in stationary regime.

The inner wall of the vessel which is above the level of the liquid medium  
20 in the vessel generally extends above the level of the liquid medium in the vessel to the top of the vessel.

According to a first embodiment of the process of the invention, the temperature of the inner wall of the vessel which is above the level of the liquid medium in the vessel is at a temperature lower than 120 °C, preferably lower  
25 than or equal to 110 °C, more preferably lower than or equal to 100 °C and most preferably lower than or equal to 90 °C.

According to a first variant of the first embodiment, the internal wall of the vessel which is above the level of the liquid medium in the vessel is cooled down by means of an external cooling system. That system can be for instance a  
30 cooling fluid circulating between the inner and outer wall of the part of the vessel (double-walled conventional jacket) which is above the level of the liquid medium in the vessel or a cooling fluid circulating in a serpentine welded on the vessel wall or connected by a thermally conductive cement or located within the protective layer (for instance serpentine flooded in the protective layer or  
35 channel drilled in the bulk of the protective layer) or a semi-shell tube (half-pipe jacket) in contact with the outer wall of the vessel which is above the level of the

liquid medium in the vessel or by flushing a cooling fluid on the outer wall of the vessel which is above the level of the liquid medium in the vessel. The cooling fluid can be a gas or a liquid. It is preferred to use a gaseous fluid when flushing the outer wall. The gas can be for example dry air or nitrogen. It is preferred to use a liquid fluid when circulating in double-walled envelope and serpentines. The liquid can be an organic liquid, an inorganic liquid or a mixture thereof. It is preferred to use an inorganic liquid, more preferably water.

According to a second variant of the first embodiment, the inner wall of the vessel which is above the level of the liquid medium in the vessel is cooled down by flushing a cooling fluid on the inner wall. The fluid can be a gas or a liquid. The gas can for instance be hydrogen chloride or steam. The temperature of the gas is lower than the temperature of the liquid medium. The fluid is preferably a liquid. The liquid can be selected from a cold condensate arising from the treatment of the vapour phase in equilibrium with the liquid medium in a distillation, evaporation or stripping column, or selected from glycerol, water, an aqueous solution of hydrogen chloride, dichloropropanol, monochloropropanediol and mixtures thereof. By cold condensate, one intends to denote a condensate which temperature is lower than the temperature of the vapour phase in equilibrium with the liquid medium.

The temperature of the cooling fluid is adjusted to obtain the inner wall temperature mentioned above.

According to a second embodiment of the process of the invention, the temperature of the inner wall of the vessel which is above the level of the liquid medium in the vessel is at a temperature at least 1 °C higher than the dew temperature of the vapour above the liquid medium, preferably at least 3 °C higher, more preferably at least 5 °C higher and most preferably at least 10 °C higher.

According to a first variant of that second embodiment, the inner wall of the vessel which is above the level of the liquid medium in the vessel is heated up by means of an external heating system. That system can be for instance a heating fluid circulating between the inner and outer wall (double-walled conventional jacket) of the part of the vessel which is above the level of the liquid medium in the vessel or a heating fluid circulating in a serpentine welded to the vessel wall or connected by a thermally conductive cement or in a semi-shell tube (half-pipe jacket) in contact with the outer wall of the vessel which is above the level of the liquid medium in the vessel or by flushing a heating fluid

on the outer wall of the vessel which is above the level of the liquid medium in the vessel. The heating of the part of the vessel which is above the level of the liquid medium in the vessel can also be carried out by using electric tracing or by radiation, such as electro-magnetic radiations like for instance Infra Red radiations. When a heating fluid is used, it can be a gas or a liquid. When a double-walled envelope or a serpentine or a semi-shell system is used for the external heating, it is preferred to use a liquid. The liquid can be an organic, an inorganic liquid or a mixture thereof. An inorganic liquid is preferred, pressurized water being most preferred. When the heating is carried out by flushing a heating fluid, the fluid is preferably a hot gas. By hot gas, one intends to denote a gas with a temperature is higher than the temperature of the liquid medium. The gas can be nitrogen, air or steam. Steam is more preferred. Steam with a pressure lower than 10 absolute bar is the most preferred.

According to a second variant of that second embodiment, the internal wall of the vessel which is above the level of the liquid medium in the vessel is heated up by means of an internal heating system and a thermally insulating device can optionally be placed on the external wall of the vessel which is above the level of the liquid medium. The internal heating is carried out by flushing a heating fluid on the inner wall. By heating fluid, one intends to denote a fluid with a temperature higher than the temperature of the liquid medium. The fluid can for instance be nitrogen, steam, hydrogen chloride or low boiling compounds produced by the reaction between glycerol and hydrogen chloride like for instance dichloropropanol, or mixture thereof. The gas can be introduced in the vessel by any suitable way, like for instance above the level of the liquid medium in the vessel in such a way that a helicoidal stream of gas is produced above that level.

The temperature of the heating fluid is adjusted to obtain the inner wall temperature mentioned above.

Any kind of thermally insulating device can be used. Insulating material can be made of inorganic material like perlite, of organic material or mixture thereof.

According to a third embodiment of the process of the invention, the inner wall of the vessel which is above the level of the liquid medium in the vessel is trickled with a liquid. The liquid can be selected from a cold condensate arising from the treatment of the vapour phase in equilibrium with the liquid medium in a distillation, evaporation or stripping column, or selected from glycerol, water,

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an aqueous solution of hydrogen chloride, dichloropropanol and monochloropropanediol, and mixtures thereof. By cold condensate, one intends to denote a condensate which temperature is lower than the temperature of the vapour phase in equilibrium with the liquid medium. The liquid can be selected  
5 from another part of the process with a low concentration of hydrogen chloride.

The various embodiments which have been described above can be combined.

According to a fourth embodiment of the process of the invention, the inner wall of the vessel which is above the level of the liquid medium in the  
10 vessel, can be heated and trickled with a liquid. In that embodiment, it is preferred to heat the upper part of the inner wall and to trickle the lower of the inner wall which is above the level of the liquid medium in the vessel. The lower part generally extends from the level of the liquid medium in the vessel to 0.1 m above that level. The upper part generally extends from 0.5 m above the  
15 level of the liquid medium to the top of the vessel.

According to a fifth embodiment of the process of the invention, the inner wall of the vessel which is above the level of the liquid medium in the vessel, can be cooled and trickled with a liquid.

The examples below are intended to illustrate the invention without,  
20 however, imposing any limitation thereon.

Example 1 (not according to the invention)

When contacted with a water-hydrogen chloride liquid mixture containing 20 % by weight of hydrogen chloride at 120°C, an enamelled-lined steel sample exhibits a corrosion rate of 0.035 mm/year.

25 Example 2 (according to the invention)

When contacted with a water-hydrogen chloride liquid mixture containing 20 % by weight of hydrogen chloride at 50°C, an enamelled-lined steel sample exhibits a corrosion rate of less than 0.010 mm/year.

CLAIMS

1. Process for the manufacture of dichloropropanol in which glycerol is reacted with a chlorinating agent comprising hydrochloric acid in a liquid medium in equilibrium with a vapour phase and in which the condensation of a  
5 fraction exhibiting the composition of the vapour phase is prevented.

2. Process for the manufacture of dichloropropanol in which glycerol is reacted with a chlorinating agent comprising hydrogen chloride, wherein, in a vessel, a liquid medium is in equilibrium with a vapour phase and wherein at  
10 least one part of the inner wall of the vessel which is above the level of the liquid medium in the vessel is maintained at a temperature lower than 120 °C or at a temperature at least 1 °C higher than the dew temperature of the vapour phase and/or is trickled with a liquid.

3. Process according to claim 2 wherein the inner wall of the vessel which is above the level of the liquid medium in the vessel is maintained at a  
15 temperature lower than 120 °C by cooling down by means of :

- (a) an external cooling system selected from a cooling fluid circulating in a serpentine or a semi-shell tube in contact with the outer wall of the vessel or by flushing a cooling fluid on the outer wall of the vessel which is above the level of the liquid medium in the vessel or
- 20 (b) an internal cooling system which consists of flushing a cooling fluid on the inner wall of the vessel which is above the level of the liquid medium in the vessel or,
- (c) both (a) and (b).

4. Process according to claim 2 wherein the internal wall of the vessel  
25 which is above the level of the liquid medium in the vessel is maintained at a temperature at least 1 °C higher than the dew temperature of the vapour phase by heating up by means of :

- (A) an external heating system selected from a heating fluid circulating in a serpentine or a semi-shell tube in contact with the outer wall of the vessel or



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by flushing a heating fluid on the outer wall of the vessel which is above the level of the liquid medium in the vessel or

(B) an internal heating system which consists of flushing a heating fluid on the inner wall of the vessel which is above the level of the liquid medium in the  
5 vessel or

(C) both (A) and (B).

5. Process according to claim 4 wherein an internal heating system is used and a thermally insulating device is placed on the external wall of the vessel which is above the level of the liquid medium.

10 6. Process according to any of claims 2 to 5 wherein the inner wall of the vessel which is above the level of the liquid medium in the vessel is trickled with a liquid selected from a cold condensate arising from the treatment of the vapour phase in equilibrium with the liquid medium in a distillation, evaporation or stripping column, or selected from glycerol, water, an aqueous solution of  
15 hydrogen chloride, dichloropropanol, monochloropropanediol and mixtures thereof.

Résultat de la recherche

23/05/2007

L2 ANSWER 1 OF 1 CA COPYRIGHT 2007 ACS on STN  
AN 109:6092 CA  
TI Preparation of chloroethyl ethers from hydroxyethyl ethers  
IN Kitamura, Satoshi; Uemura, Shoji; Hida, Takashi  
PA Nisso Petrochemical Industries Co., Ltd., Japan  
SO Jpn. Kokai Tokkyo Koho, 5 pp.  
CODEN: JKXXAF  
DT Patent  
LA Japanese  
FAN. CNT 1

|      | PATENT NO.  | KIND | DATE     | APPLICATION NO. | DATE         |
|------|---|------|----------|-----------------|--------------|
| PI   | JP 62242638   | A    | 19871023 | JP 1986-85692   | 19860414 <-- |
| PRAI | JP 1986-85692   |      | 19860414 |                 |              |
| AB   | RCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> Cl (I; R = OH, Cl) were prepared by treating RCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH (II) with HCl in the presence of carboxylic acids to control formation of HOCH <sub>2</sub> CH <sub>2</sub> OH which was hard to sep. from the products. Thus, HCl was introduced into a mixture of 106 parts II (R = OH) and 2.3 parts caproic acid at 110° for 10 h to give I (R = OH) at 80.3% conversion and 48.4% selectivity. |      |          |                 |              |

Résultat de la recherche

23/05/2007

L1 ANSWER 1 OF 1 WPIDS COPYRIGHT 2007 THE THOMSON CORP on STN  
AN 1987-338139 [48] WPIDS  
DNC C1987-144454 [21]  
TI High yield, selective preparation of chlorinated ether(s) - by treating  
corresp. alcohol(s) with hydrogen chloride in presence of carboxylic  
acid(s)  
DC B16  
IN HIDA T; KITAMURA S; UEMURA S  
PA (NISS-N) NISSO YUKA KOGYO KK  
CYC 1  
PIA JP 62242638 A 19871023 (198748)\* JA 5[0] <--  
ADT JP 62242638 A JP 1986-85692 19860414  
PRAI JP 1986-85692 19860414  
AN 1987-338139 [48] WPIDS  
AB JP 62242638 A UPAB: 20050426  
Preparation of chlorinated ether of formula  $RCH_2CH_2OCH_2CH_2Cl$  (I) is effected  
by  
chlorinating ether  $RCH_2CH_2OCH_2CH_2OH$  (II) with hydrogen chloride in  
presence of carboxylic acid. R = OH or Cl.  
Pref. 1-15 aliphatic- or 6-15C alicyclic- or 7-15C aromatic-cpd. with one  
or more carboxyl gps., i.e., mono- and/or poly-carboxylic acid, amino  
acid, acid anhydride or ion-exchange resin etc. are used to obtain (I)  
selectively. Ratio of (III)/(II) is 0.1-10 weight%, especially 0.5-5 weight%.  
Chlorination is carried out at 50-150 deg. C, especially 80-120 deg. C by  
using  
gaseous hydrogen chloride in presence of (III) and accelerator, Lewis  
acids such as aluminum chloride, zinc chloride etc.  
USE/ADVANTAGE - (I) is useful as intermediate to various chemicals.  
High purity (I) is prepared by simple procedure in high yield and  
selectivity by using (III) in chlorination.